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Characterization of Individual Fly Ash Particles Emitted from Coal- and Oil-Fired Power Plants

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16. ABSTRACT

Individual particles from coal- and oil-fired power plants were analyzed by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer to investigate the morphology and composition as a function of size. Samples were collected on filters by a dichotomous sampler in the fine (< 2.5 μm aerodynamic diameter) and the coarse fractions (2.5 to 5-10 μm). In both fractions coal fly ash particles were predominantly smooth spheres, and no cenospheres (perforated hollow spheres) were detected. Almost 90% of the mass concentration occurred in the coarse fraction; the major elements included Al, Si, K, Ca, Ti, and Fe. Sulfur appeared as a surface layer on the mineral core. The abundances of Fe and S in each particle were highly variable. The ratio of Al to Si was fairly constant for most of the spheres but not for the relatively few Fe-rich or non-spherical coal fly ash particles. Over 90% of the mass of oil fly ash occurred in the fine fraction. The compositions of individual oil fly ash particles were highly variable, and the distribution of chemical and morphological properties of individual particles vs. diameter was found to be trimodal. Particles smaller than 0.7 μm were irregularly shaped and relatively pure in sulfate. Particles in the 0.7 to 3 μm range were predominantly spherical and of mineral composition, highly variable in Al, Si, P, Ca, Ti, and Fe. Larger particles had a lacy morphology and consisted of carbonaceous material and sulfur. In about half of the oil fly ash particles analyzed, V and/or Ni were detected.

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CHARACTERIZATION OF INDIVIDUAL FLY ASH PARTICLES EMITTED FROM COAL- AND OIL-FIRED POWER PLANTS

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Abstract—Individual particles from coal- and oil-fired power plants were analyzed by a scanning electron microscope equipped with an energy dispersive X-ray spectrometer to investigate size, morphology, and composition. Samples were collected on filters by a dichotomous sampler in the fine (< 2.5 μm aerodynamic diameter) and coarse (2.5 to 5–10 μm) fractions. In both fractions coal fly ash particles were predominantly ($> 95\%$) smooth, mineral spheres. No cenospheres (perforated hollow spheres) were detected, and almost 90% of the mass concentration occurred in the coarse fraction. Sulfur appeared as a surface layer on the mineral core; the abundances of Fe and S were highly variable. The Al/Si ratio was fairly constant for most of the spheres but not for the relatively few Fe-rich or non-spherical coal fly ash particles. Over 90% of the mass of oil fly ash occurred in the fine fraction. The size distribution of chemical and morphological properties of individual oil fly ash particles was found to be trimodal. Oil fly ash particles smaller than 0.7 μm (geometric diameter) were non-spherical and relatively pure in sulfate, and 90% of such particles were smaller than 0.5 μm; V or Ni could be detected in 50% to 60% of such particles larger than 0.3 μm. Those particles in the 0.7–3 μm range of geometric diameters were predominantly spherical and of mineral composition, highly variable in Al, Si, P, Ca, Ti and Fe; 50–60% of them contained detectable amounts of V or Ni. Larger oil fly ash particles had a lacy morphology and consisted of carbonaceous material and sulfur.

Key word index: Aerosol composition, coal-fired power plants, coal-fly ash, electron microscopy, fly ash, individual particles, oil-fired power plants, oil fly ash, receptor model, scanning electron microscopy, X-ray analysis.

INTRODUCTION

In a 1982 study of aerosol in the Philadelphia airshed, samples from point sources and ambient air were analyzed in order to evaluate the ability of receptor models to determine the impacts of emission sources on air quality. The sources sampled were oil- and coal-fired power plants, a municipal refuse incinerator, a refinery, an aluminum furnace, an antimony roasting plant (Houck *et al.*, 1986) and soil dust. The ambient samples were collected at three sites along a line that crosses the urban area and is along the direction of prevailing winds. Dichotomous samplers were used to collect both the source and ambient samples. The present report describes the application of electron microscopy to characterize individual fly ash particles emitted from oil- and coal-fired power plants. An objective of this characterization was to identify chemical and morphological features that could enable particles from ambient air to be classified by source type.

Power plant emissions have been the subject of several previous studies (Hansen *et al.*, 1984; Bacci *et al.*, 1983; Cheng *et al.*, 1976; Natusch *et al.*, 1974, for example). Some of these studies used analytical techniques applied to bulk samples, which resulted in averaging the chemical composition of large and small particles. In a few studies, individual fly ash particles were analyzed with electron microscopy techniques, but only particles larger than a few μm in diameter were studied (Linton *et al.*, 1977; Hulett *et al.*, 1980; Hock and Lichtman, 1983). In the present work we extend the study of individual fly ash particles to the 0.2- to 5-μm size range. Such particles are important because they are respirable, they can be transported hundreds of km, sulfate formation may occur on their surfaces (Mamane and Pueschel, 1979; Mamane, 1984), and they contain higher concentrations of toxic elements (Natusch *et al.*, 1974).

We used a scanning electron microscope (SEM) equipped with an energy dispersive X-ray analyzer (EDX) to study the elemental content, size and morphology of individual particles in fly ash samples collected in one coal-fired power plant and two oil-fired power plants in Philadelphia. The coal-fired power plant was operated at full load (300 MW) during sample collection; it was equipped with an electrostatic precipitator (ESP) that was not fully operational when our samples were collected. One of the oil-fired power plants had a 600-MW capacity and was operated at 460 MW; it was equipped with a

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cyclone for emissions control. The other oil-fired power plant had a 395-MW capacity and was equipped with an ESP. Because the sampling points were downstream from any control devices, the collected samples can be expected to represent particles emitted into the atmosphere.

The samples were collected in a sampling train consisting of a stack probe, a dilution chamber, and a Sierra dichotomous sampler (Cooper *et al.*, 1984; Houck *et al.*, 1986). In the dilution chamber, 140–350°C hot stack gases were diluted by a factor of 30–40 with filtered ambient air, which reduced the temperature to 25–35°C. The dichotomous sampler collected particles in two size ranges: fine (< 2.5-μm aerodynamic equivalent diameter) and coarse (> 2.5 μm). The upper limit for the coarse fraction was not precisely defined but was limited by the stack probe and sampling lines to 5–10 μm (Cooper *et al.*, 1984). The collection surfaces were 2-μm pore size Teflon filter (Membrana Corp.) for the fine fraction and 0.3-μm pore size Nuclepore filter for the coarse fraction. Such filters have been shown to be highly efficient for particles as small as 0.035 μm (Liu *et al.*, 1983). Because fine particles are not inertially separated from the airstreams in a dichotomous sampler and because 10% of the sampled air flows through the coarse-fraction filter, 10% of the fine particles plus all of the coarse particles are collected on the coarse-fraction filter. Each Nuclepore filter was precoated with about 25 $\mu g\,cm^{-2}$ of mineral oil to prevent loss of coarse particles (Dzubay and Barbour, 1983). Prior to our analysis by SEM, the samples' bulk elemental composition was determined by X-ray fluorescence (XRF) and reported by Cooper *et al.* (1984); the XRF results for the samples that we analyzed by SEM–EDX are shown in Table 1. In other sets of samples, the bulk compositions were determined by XRF, neutron activation, ion chromatography, and pyrolysis and reported by Houck *et al.* (1986).

EXPERIMENTAL PROCEDURE

A 4 by 4 mm piece was cut from each sample for analysis by SEM–EDX and was coated under vacuum with a thin layer of carbon to prevent charging. The coated filter was placed in an Amray Model 1000 scanning electron microscope, which was operated under the following conditions: 30-kV accelerating voltage, 100-μA beam, 26-degrees stage tilt, and 12-mm working distance. The incident spot size of the electron beam was approximately 0.01 μm, but scattering and penetration caused X-ray signals to be emitted from a hemisphere about 1 μm in radius. Elements heavier than Na were detectable by EDX when their mass concentrations in a particle exceeded 1%. Elements lighter than Na were not detected by EDX, but if a particle was composed almost completely of lighter elements, that fact could be ascertained from the relatively high background in its X-ray spectrum.

For each sample, 5–10 random fields of view were chosen, and all the discernable particles in each field (typically 10–30) were analyzed manually. For each particle, an X-ray spectrum was taken, and particle size and special morphological features were recorded. Although our manual analysis is more tedious and time-consuming than an automated procedure (Lee and Kelly, 1980), manual analysis provides a reliable way to ascertain that the information obtained applies to individual particles and not to doublets or aggregates. In several cases X-rays were obtained from 2 or 3 points on a particle in order to identify any inhomogeneities in composition.

Table 1. Elemental concentrations and sample masses for size-fractionated samples from cyclone and ESP-controlled oil-fired power plants and from an ESP-controlled coal-fired power plant*

	Concentration in $mg\,g^{-1}$				Coal species concentration ratios
	Oil, fine		Coal		
	Cyclone	ESP	fine	coarse	fine/coarse
Al	20	15	139	139	1
Si	34	28	213	221	1
P	10	21	6.9	2.2	3
S	144	133	49	6.3	8
K	2	2	11	14	1
Ca	18	32	12	15	1
Ti	1	<0.3	9.0	10	1
V	14	10	0.9	0.7	1
Cr	0.5	0.6	0.6	0.5	1
Mn	0.3	0.5	0.4	0.5	1
Fe	17	23	75	94	1
Ni	20	22	0.4	0.4	1
Cu	1	1	0.3	0.3	1
Zn	8	18	0.9	0.5	2
As	0.3	0.3	0.9	0.4	2
Se	0.03	0.02	0.6	0.03	20
Pb	9	25	0.5	0.3	2
Sample mass (μg)	AF146 178	AF158 190	AF143 316	CC086 2055	

* The data are from Cooper *et al.* (1984).

RESULTS AND DISCUSSION

Coal fly ash

Figures 1(a) and 1(b) are typical micrographs of coal fly ash particles in the coarse and fine fractions, respectively. The largest particle diameter observed in the fine fraction was about 1.5 μm; for a sphere having an assumed density of 2.7 g cm^{-3}, this corresponds to an aerodynamic equivalent diameter of 2.5 μm, which is the upper limit of the fine fraction. The smallest size analyzed was about 0.2 μm. Any smaller particles would be masked on the Nuclepore filter by the mineral oil coating and would be masked on the Teflon filter by the structure of fibrous Teflon [Fig. 1(c)]. Consistent with a dichotomous sampler's characteristic that causes 10% of the fine-particle sample to be

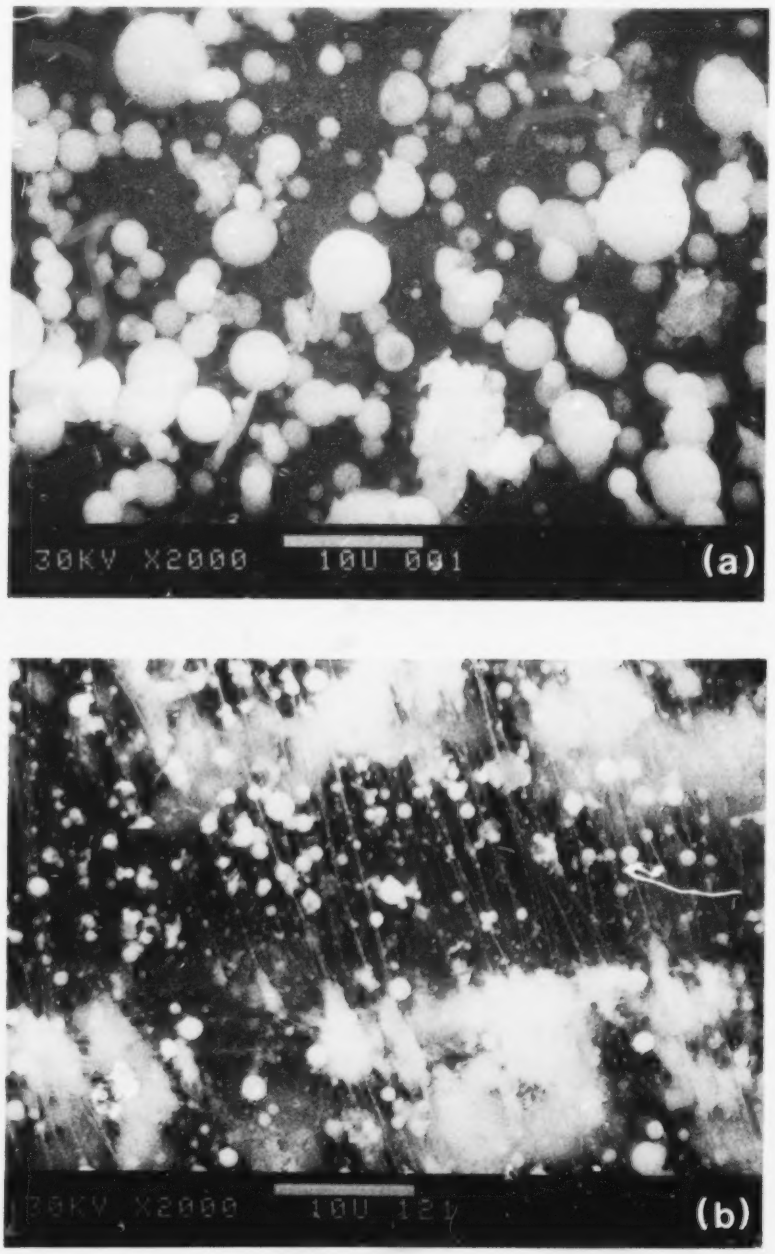

Fig. 1. (a)–(b).

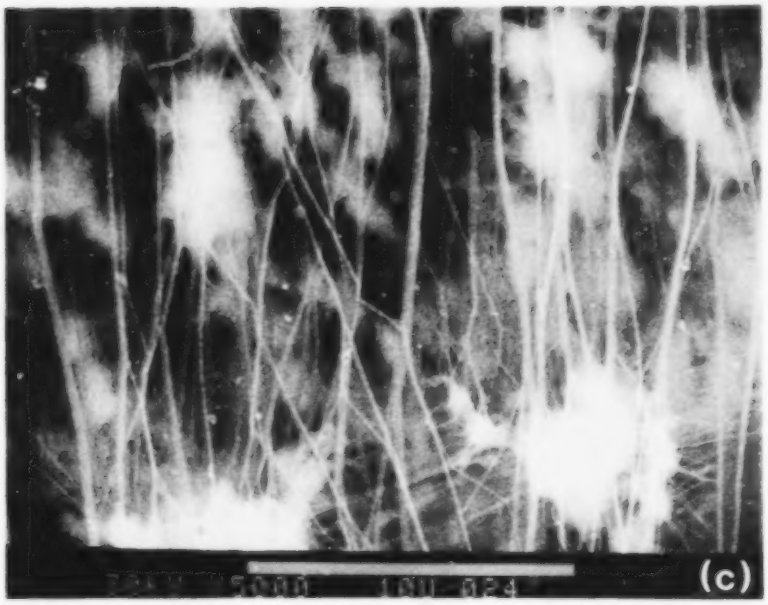

Fig. 1. Micrographs of coal fly ash particles collected in the (a) coarse particles on Nuclepore and (b) fine particles on Teflon filter. (c) Clean Teflon filter. Bars are 10 μm.

collected on the coarse-fraction filter, particles smaller than 1 μm are conspicuous on the coarse particle filter shown in Fig. 1(a).

In both the fine and coarse fractions, over 95% of the coal ash particles were spheres having rather smooth surfaces. Examination of several hundred particles revealed no differences in shape or surface morphology between the fine and the coarse fractions. Such a predominance of spherical particles is also apparent in the micrographs of coal fly ash particles reported by Cheng *et al.* (1976) and Henry and Knapp (1980). However, the atlas of McCrone and Delly (1973) indicates that nonspherical particles can predominate in some coal ash samples.

X-ray spectra of representative coal fly ash particles are shown in Fig. 2 and indicate heterogeneity in elemental content. Figure 2(A) shows the spectrum of a typical coal fly ash particle, which consists mainly of Al, Si, and Fe, with smaller amounts of S, K, Ca and Ti. Such a particle has a characteristic aluminosilicate and iron matrix (Al, Si, Fe and 0). Its composition is qualitatively similar to that of the bulk composition of coal fly ash shown in Table 1. Figures 2(B) and 2(C) are spectra of atypical particles for which Fe and Ca are the most abundant elements. Other atypical coal fly ash particles were found to consist primarily of Ti. Other elements that were detected in some of the particles were Mg, P, Cr and Zn. Of the few nonspherical particles that were observed, some were composed of the typical aluminosilicate and iron matrix, and others contained iron but had a high background indicative of carbonaceous material.

To show the variability of the major elements in individual coal fly ash particles, X-ray intensity ratios vs diameter are plotted in Figs 3, 4 and 5. An interesting feature of Figs 3–5 is that several 'coarse' particles have geometric diameters smaller than 2.5 μm, the lower aerodynamic equivalent diameter limit for the coarse fraction. Some may be dense minerals that have geometric diameters that are substantially smaller than their aerodynamic equivalent diameters; others represent the 10% of the fine particles collected on the coarse-fraction filter. To a first approximation, the X-ray intensity for an element in a particle is proportional to its concentration in the particle. For more exact results, the X-ray intensities need to be corrected for absorption and fluorescence effects (Heinrich, 1980 and references therein). Such corrections are most needed when fine and coarse particles are compared with each other because the entire volume of a fine particle can be sensed by EDX, but only a portion of a large one is sensed. The problem of relating sensitivity to mass is even more complex for particles having a core and a surface coating that differ in composition.

Figure 3 shows the Al/Si X-ray intensity ratios for individual particles in the fine and coarse fractions. The most frequently occurring ratio is 0.7 (in close agreement with the bulk compositional ratios shown in Table 1). For individual particles, 85% of the ratios range from 0.5 to 1; 14% of the particles have ratios below that range, and many of those were highly enriched in Fe, suggesting that Fe replaced Al in the aluminosilicate matrix.

Figure 4 shows the Fe/Si X-ray intensity ratio vs

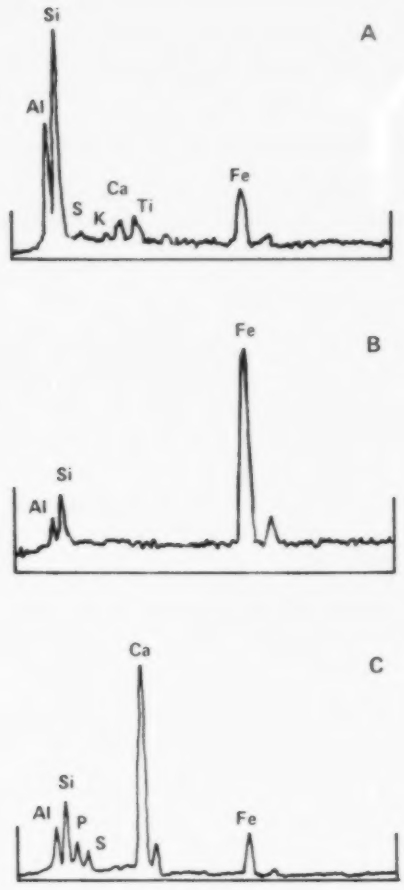

Fig. 2. X-ray spectra of individual coal fly ash particles representing (A) typical aluminosilicate particle, (B) atypical Fe-rich particle, and (C) atypical Ca-rich particle.

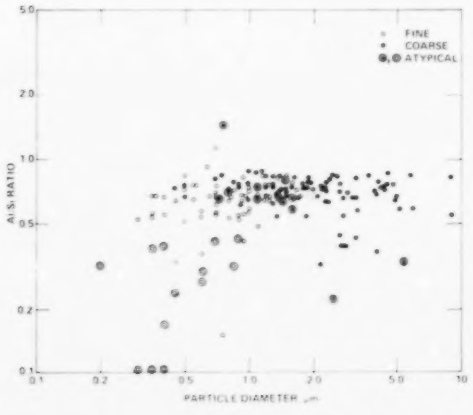

Fig. 3. The Al/Si X-ray intensity ratio as a function of geometric particle diameter for individual fine and coarse coal fly ash particles.

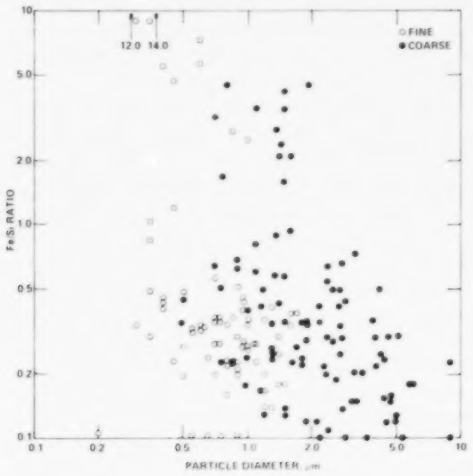

Fig. 4. The Fe/Si X-ray intensity ratio as a function of geometric particle diameter for individual coal fly ash particles.

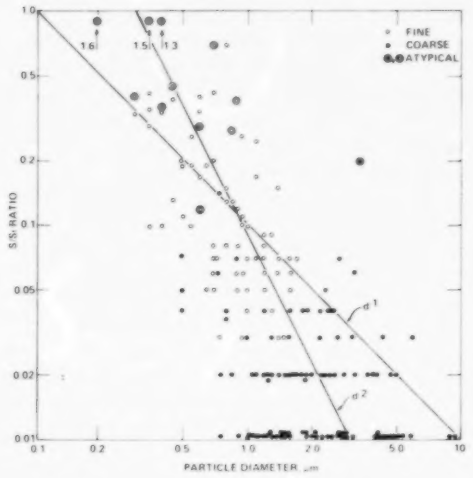

Fig. 5. The S/Si X-ray intensity ratio as a function of geometric particle diameter for individual coal fly ash particles. Lines representing d^{-1} and d^{-2} are plotted.

diameter for individual coal fly ash particles. The most frequently occurring ratio is 0.4 (in close agreement with the bulk composition ratios indicated in Table 1). For individual particles 85% of the ratios range from 0.1 to 3; such a range of variation is much larger than that for the Al/Si ratio. The Fe/Si X-ray intensity ratio exceeded 1 for about 10% of the particles smaller than 2 μm; none of the larger particles were so highly enriched in Fe. When such highly enriched fine particles are observed in ambient air, they could mistakenly be attributed to some other source type such as an iron smelter, if the results of Fig. 4 were ignored.

Hock and Lichtman (1983) have investigated the iron abundance of 5- to 30-μm fly ash particles at a coal-fired power plant and in the plume 15 km downwind. They found that Fe-rich particles were abundant in the stack emissions but were sparse in the plume. They attributed the low downwind abundance of Fe-rich particles to gravitational sedimentation caused by their high specific gravity. We cannot compare our results with the 5- to 30-μm data of Hock and Lichtman because only five particles (3%) in our sample were larger than 5 μm. However, in our sample, as noted above, the highest Fe/Si ratios occurred in particles smaller than 2 μm. Such small Fe-rich particles have very small gravitational settling velocities and are likely to be transported large distances.

Figure 5 shows that the S/Si X-ray intensity ratio varies dramatically with diameter, and the smallest fly ash particles are the most highly enriched in S. Such a size dependence is consistent with coal fly ash particles existing as a surface layer containing volatile elements, such as S, and a mineral core (Natusch *et al.*, 1974; Biermann and Ondov, 1980). That structure is a consequence of the coal combustion process, which pyrolyzes C and S from each coal particle while mineral matter is retained as a molten sphere; after cooling, some of the S is redeposited on the resolidified mineral core. Studies of coal power plant plumes (Mamane and Pueschel, 1979) and a study in a rural area affected by emissions from power plant plumes (Mamane, 1984) showed that individual coal fly ash particles were coated with a thin layer of sulfate. For coal fly ash particles larger than 5 μm, Linton *et al.* (1977) and Hock and Lichtman (1983) used Auger electron spectroscopy and ion beam depth profiling to show that S was concentrated on a surface layer a few nm thick. The discussion below suggests that this conclusion is valid for smaller particles also.

Biermann and Ondov (1980) evaluated aerosol models for the deposition of a surface layer onto a solid core. For a thin layer on a particle of diameter d, they showed that the concentration C can be expressed as

$$C = C_c + Kd^{-n} \quad (1)$$

where C_c is the concentration in the core, and K is approximately a constant. The exponent n is determined by the mechanism for mass transfer to a particle's surface. The slip flow and transition regions of aerosol mechanics were shown to result in dependences of d^{-2} and d^{-1}, respectively. Biermann and Ondov showed that a d^{-2} dependence best describes the bulk concentrations of As and Se in size-fractionated coal fly ash samples in particles larger than 0.2 μm. If we assume that fly ash S occurs only as a thin layer over a Si-containing mineral core, Equation (1) implies that the S/Si concentration ratio is proportional to d^{-n}. In Fig. 5 we plot lines representing d^{-1} and d^{-2}. It is clear that the d^{-2} dependence best describes the S/Si X-ray intensity ratios.

It is of interest to compare the XRF results of the bulk coal fly ash samples (Cooper *et al.*, 1984) shown in Table 1 with the SEM–EDX results for individual particles. The last column in Table 1 gives the ratios of the fine to coarse species concentrations from the bulk analysis. The ratios indicate no pronounced dependence of concentration on particle size for the mineral elements such as Al, Si, K, Ca, Ti and Fe, and trace elements such as Cr, Mn, Ni and Cu. Elements having concentrations that increase with decreasing particle size include P, S, Zn, As, Se and Pb. Other studies have shown similar grouping, although some minor differences do exist (Coles *et al.*, 1979, and references therein; Linton *et al.*, 1977; Natusch *et al.*, 1974). The XRF data in Table 1 indicate that the largest fine-particle enrichments occur for S and Se. As noted above, our SEM–EDX data in Fig. 5 also indicate such an effect for S.

Oil fly ash

Our examination of several hundred particles by SEM/EDX revealed that the distribution of morphological and chemical properties vs size was trimodal. Figure 6 shows micrographs that illustrate the morphological features of particles in each mode, and Fig. 7 shows their typical X-ray spectra. Table 2 shows the distribution of particles in the middle and small modes according to V, Ni, S and mineral content. Particles are classified as S-rich or mineral depending on whether or not the S peak height exceeded by a factor of two the others in the X-ray spectrum.

The coarse mode contains particles larger than 3-μm geometric diameter, which have a lacy or spongy appearance similar to those reported by others (McCrone and Delly, 1973; Cheng *et al.*, 1976; Bacci *et al.*, 1983). Figure 6(a) illustrates the morphology of a typical large lacy particle in our sample. Figures 7(A) and 7(B) illustrate X-ray spectra for two lacy particles and indicate that such particles are S-rich. The relatively high X-ray background for such large particles indicates a carbonaceous nature. The micrographs in Fig. 6 indicate that lacy particles comprise a very small fraction of the total number of particles collected.

Table 2. Classification of fine particles in two geometric size ranges from oil-fired power plants

Particle type*	Ni or V detected	Percent abundance by number: 0.3–0.7 μm ($N = 31$)	Percent abundance by number: 0.7–2.7 μm ($N = 82$)
A. S-rich	neither	42 ± 14	6 ± 3
B. S-rich	one	45 ± 15	2 ± 2
C. S-rich	both	10 ± 6	6 ± 3
D. mineral	neither	< 3	30 ± 7
E. mineral	one	< 3	29 ± 7
F. mineral	both	3 ± 3	26 ± 6

* Particles were classified as S-rich if the S peak area exceeded by a factor of 2 the peak area for each of the following: Mg, Al, Si, P, Ca, Ti and Fe. Otherwise, particles were classified as mineral.

Figures 6(b) and 6(c) illustrate that the middle mode consists mostly of 0.7–3 μm smooth spheres that are similar in appearance to coal fly ash. Typical X-ray spectra in Figs 7(C) and 7(D) indicate a mineral-like composition. Examination of the X-ray spectra of over 80 mineral particles indicated that the abundances of the mineral elements (Mg, Al, Si, P, Ca, Ti and Fe) were highly variable and that either V or Ni could be detected in about 50–60% of the particles (see Table 2). The distribution by elemental profile of particles in the

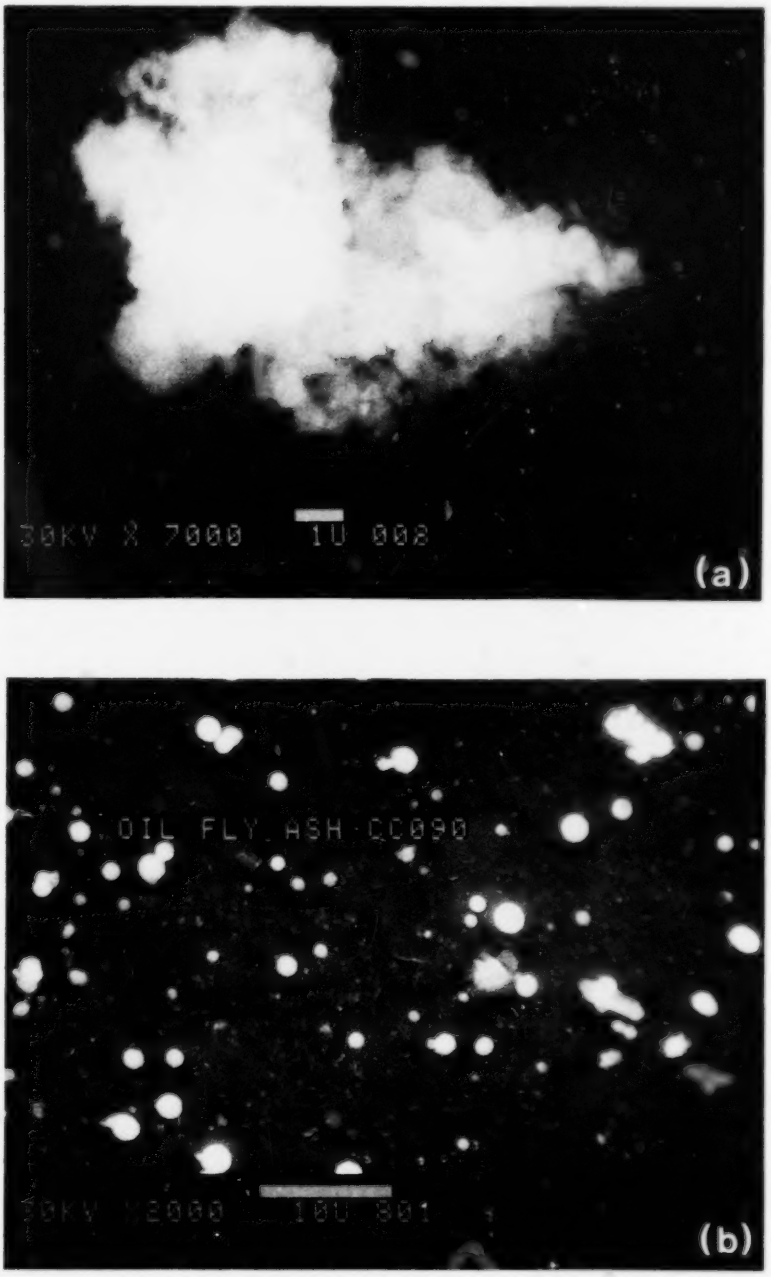

Fig. 6. (a)–(b).

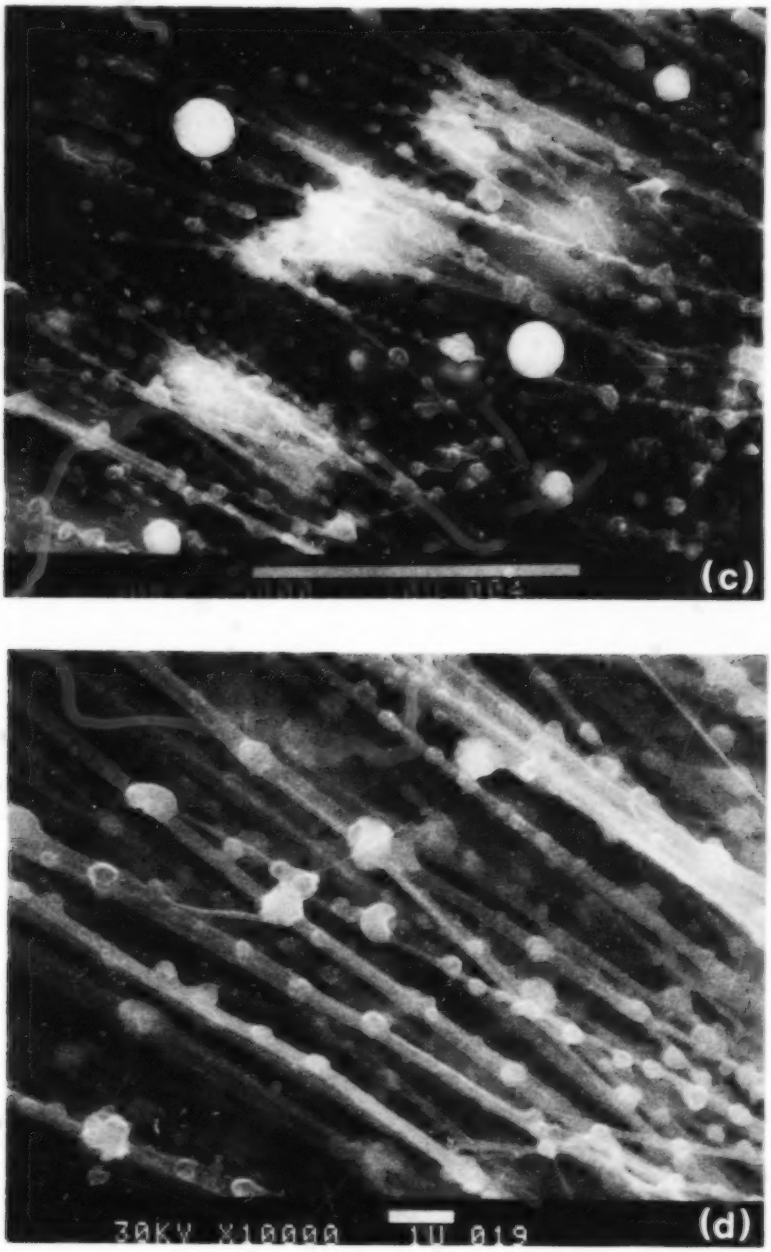

Fig. 6. Micrographs of oil fly ash particles from a cyclone-controlled power plant showing (a) coarse mode lacy particle on a Nuclepore (7000X), (b) coarse mode lacy particles and intermediate mode spherical particles on Nuclepore (2000X), (c) fine and middle mode spherical particles on Teflon (5000X), and (d) small mode non-spherical particles on Teflon (10,000X).

0.7–3 μm range of geometric diameter was 70–80% mineral, 10–20% S-rich crystalline matter and less than 10% lacy particles.

The small particle mode is illustrated in Fig. 6(D) and consisted of nonspherical submicrometer particles. The X-ray spectra in Figs 7(E) and 7(F) illustrate that these particles were S-rich. V or Ni were detectable in about 50–60% of these particles. Particles in this mode collected on a Nuclepore filter were analyzed for sulfate by a $BaCl_2$ microspot technique (Mamane and

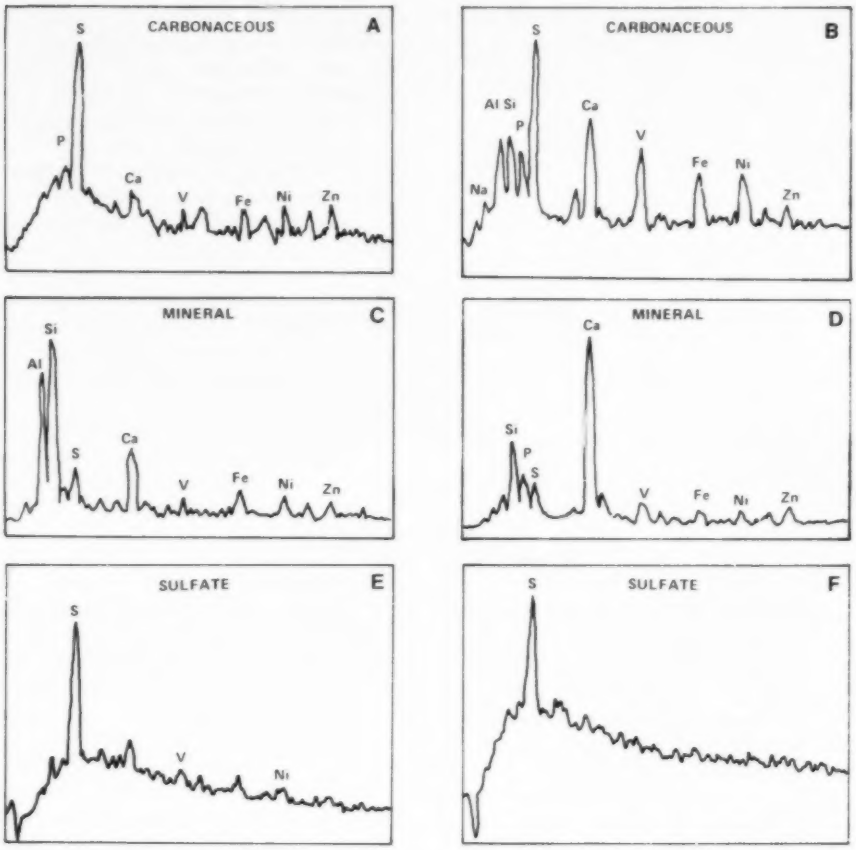

Fig. 7. X-ray spectra of individual oil fly ash particles representative of (A–B) coarse mode lacy particles, (C–D) intermediate mode mineral spheres, and (E–F) small mode S-rich non-spherical particles.

de Pena, 1978). Although this technique was originally designed to be used in conjunction with a transmission electron microscope, we have observed the reaction spots with a SEM, and the results indicate that almost all the small particle mode consists of water-soluble sulfates. Such a finding is consistent with the bulk composition results of Henry and Knapp (1980) and Houck *et al.* (1986) for oil-fired power plants. The sample loadings were sufficiently high for the soluble sulfate particles to congeal on the filter causing the observed sizes to be larger than the original ones. Over 90% of the S-rich particles were smaller than 0.5 μm; their original sizes before congealing on the filter may have been even smaller.

We offer the following explanation for the existence of the three modes: the small particle mode results from nucleation and coagulation of sulfuric acid produced by burning the S in the fuel. The middle mode consists of the mineral inclusions in the residual oil that resolidified after the fuel was burned. The large particle mode consists of incompletely burned hydrocarbon. The S in middle and upper mode particles is a likely consequence of chemical and physical surface reactions that occur during and after combustion.

Comparison of coal and oil fly ash

The bulk compositions of oil and coal fly ash particles with C content (Houck *et al.*, 1986) and estimated oxygen included are compared in Table 3. The mineral component includes the oxides of Al, Si, P, Ca, Ti, Mn and Fe. The 'sulfate, cation, and water' component represents the S concentration multiplied by 5 ± 1. Such a range includes the values 4.1 and 6 that would result from S being in the forms of ammonium sulfate and H_2SO_4 (weighed at 40% r.h.), respectively. The presence of major amounts of other metal salts of S is precluded by the relatively low abundance of the metals shown in Table 1. The species in Table 3 account for 100% of the total mass within an accuracy of 15%. The data indicate that mineral matter accounts for over 80% of coal ash and only 20–25% of oil fly ash. In contrast, sulfate and its related cations and water account for about 20% of coal fly ash and 70% of oil fly ash. The minor components As and Se

Table 3. Mass balance for fine fraction particles from coal- and oil-fired power plants

Component	Abundance (mg g^{-1}) Oil ESP	Oil Cyclone	Coal
Carbon*	14	102	8
Mineral†	207	256	889
As	0.3	0.3	0.9
Se	<0.1	<0.1	0.6
Sulfate, cation and water‡	720	665	240
VO_2^+	23	16	1
NiO	25	28	1
ZnO	10	22	1
PbO	10	27	1
Total	1009	1116	1143

* Elemental carbon plus 1.3 times organic carbon.
† Element abundances are expressed as Al_2O_3, SiO_2, PO_4^{3-}, $CaCO_3$, TiO_2, MnO_2 and Fe_2O_3.
‡ Sulfur concentration times five. See the text for an explanation.

are enriched in coal fly ash; V, Ni, Zn and Pb are enriched in oil fly ash.

The size distributions of coal and oil fly ash are also quite different. The coarse fraction of coal fly ash accounted for about 90% of the total mass, whereas for oil fly ash the coarse fraction accounted for less than 10%. Such results are consistent with the typical size distributions for coal- and oil-fired plants summarized by Van Buren *et al.* (1985).

The SEM–EDX observations indicate that a unique feature of coal fly ash is the combination of spherical shape and aluminosilicate matrix. Such a feature may enable SEM–EDX to discriminate against soil and natural mineral particles, which have irregular shapes (McCrone and Delly, 1973). The possible tracer elements, As and Se, were not detected by EDX.

Whereas coal fly ash particles in the 0.2–10 μm size range mainly had spherical morphology and mineral composition, oil fly ash particles in that size range were quite heterogeneous, and their distribution was trimodal. Coarse oil fly ash particles were mainly of a lacy, carbonaceous nature. Within the fine fraction, the compositions of oil fly ash particles changed at 0.5–0.7 μm diameter. Smaller particles consisted mainly of S and associated lighter elements, as typified by Figs 7(E) and 7(F), whereas 0.7–3 μm particles were mainly minerals having smooth spherical morphology. Although V and Ni were enriched in the bulk composition of oil fly ash, only 50–60% of the particles that we analyzed contained detectable amounts of one or both of those elements. The mineral spheres containing no detectable V or Ni would be difficult to distinguish from coal fly ash.

SUMMARY AND CONCLUSIONS

The main findings of this study are as follows: (a) coal fly ash particles are mainly alumino–silicate spheres that are somewhat variable in composition and are coated with a surface layer of sulfate. Although other investigators have reported the occurrence of cenospheres (perforated hollow spheres) as a distinctive feature of very large coal ash particles, we detected no such spheres in the 0.2–10 μm range. However, our SEM observations do not exclude the possibility of bubbles within the spheres. (b) Oil fly ash particles have a trimodal distribution of composition and morphology vs size. Large particles (>3 μm geometric diameter) have a spongy or lacy appearance and are rich in carbonaceous material and S. Particles in the middle mode (0.7–3 μm geometric diameter) oil fly ash occur mainly as mineral rich spheres. The small particle mode consists mainly of nonspherical <0.7-μm sulfate particles.

In receptor modeling applications, the use of SEM–EDX to study the characteristics of individual coal and oil fly ash particles can be a useful complement to the bulk compositional data obtained by XRF. Because the bulk composition of coal fly ash is similar to that of the earth's crust, it is difficult to use only bulk compositional data to resolve coal fly ash from soil dust. Although Se is a potential tracer for coal fly ash, its concentration is enriched mainly in the fine fraction, yet most of the total fly ash mass occurred in the coarse fraction. The use of SEM–EDX to detect mineral-rich spheres could be a powerful means of determining the contribution of coal fly ash to ambient air. However, as a prerequisite it will be necessary both to determine the abundance (if any) of mineral-rich spheres in surface soils and to establish the extent to which other industrial sources emit mineral-rich spheres.

The large variability among compositions of individual oil fly ash particles will greatly complicate the application of SEM–EDX to quantitative receptor modeling. Some oil fly ash particles observed at sources in Philadelphia were mineral-rich spheres that resembled coal fly ash. The potential distinguishing tracers V and Ni were detected in only about 50–60% of the particles analyzed.

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